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TECHNIQUES FOR THE FABRICATION OF LITHIUM DRIFTED GERMANIUM GAMMA DETECTORS

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William L. Hansen and Blair V. Jarrett

August 7, 1964

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ABSTRACT

Many new problems are encountered in attempting to apply silicon lithium drifting technology to germanium. Lithium is much more mobile in germanium and its equilibrium solubility at room temperature can be less than the acceptor concentration. The low intrinsic temperature requires drifting at low temperatures and large currents and this is frustrated by the lower thermal conductivity of germanium. Large crystals of germanium are also very fragile and are easily damaged by thermal or mechanical shock. However, techniques developed in this laboratory have permitted the manufacture of a large number of detectors with depletion depths to 1 cm, depleted volumes to 7 cm^3 and energy resolution on 100 keV γ's as good as 2.1 keV F.W.H.M. These techniques are described and some results obtained using the detectors are presented.

INTRODUCTION

The usefulness of germanium as a gamma-ray spectrometer has been demonstrated by Webb and Williams[1] and Ewan and Tavendale.[2] Germanium lithium-drifted detectors have a gamma-ray absorption coefficient of from 1 to 100% depending on energy and detector thickness,[3] a charge collection time of from 10 to 30 μsec and a gamma line width as small as 2 keV.[4] However, these detectors have not as yet become generally available to experimenters due apparently to difficulties in producing thick junctions and also to deterioration when stored under normal ambient conditions.

It is often found that lithium alloyed to p-type germanium does not produce a rectifier at room temperature or alternatively after a short time the junction loses its rectifying properties. Frequently a good junction seems to contain only immobile lithium since, on heating and reverse biasing, no lithium drifting occurs. On occasion, drifting proceeds normally for some time, then the junction disappears or it becomes a very poor rectifier. These effects are all partly understandable from the nature of the Ge-Li system -- a system which has been discussed extensively in the literature.

THE GERMANIUM-LITHIUM SYSTEM

Interest in the Ge-Li system as a tool for the study of solid solutions resulted in the work of Reiss, Fuller and Morin at Bell Telephone Laboratories and the excellent article summarizing their work up to 1956.[5] This section draws largely on their data and attempts to select information of interest to the detector area.

Lithium in germanium is of interest due principly to the fact that lithium is electrically active in germanium with only a single ionization state and that it has a mobility which is very high at temperatures at which most other defects and impurities can be considered immobile. This has allowed a demonstration of the application of a law of mass action for ions in semiconductors and has led to a better understanding of the electrical nature of lattice defects in solids.

In the absence of acceptors, lithium has a maximum solubility in germanium of about $3 \times 10^{18}/cm^3$ at 610°C and an equilibrium solubility of $6.6 \times 10^{13}/cm^3$ at 25°C.[5] The presence of acceptors increases the room temperature solubility

due to ion pairing. However, the relationship between acceptor concentration and lithium solubility is such that it is impossible to permanently maintain enough ionized lithium in the lattice to convert the germanium to n-type under equilibrium conditions at room temperature unless the acceptor concentration is less than about $5 \times 10^{14}/cm^3$. Also, as the temperature is increased above 25°C, the maximum acceptor concentration which can be overcompensated by ion-pairing and lithium solubility is reduced. This has the effect that at 60°C or higher, germanium cannot be made to have an equilibrium n-typeness due to lithium doping -- it will be either intrinsic or p-type. Fig. 1 shows a plot of intrinsic carrier concentration[7] and the solubility of lithium[5] as a function of reciprocal temperature. It is seen that, below about 57°C, germanium which has been saturated with lithium will show extrinsic n-type conduction while above this temperature it gives intrinsic conduction.

The above comments apply only to equilibrium conditions; it is, of course, possible for germanium to be super-saturated with lithium and remain n-type for fairly long periods of time even in the presence of large acceptor concentrations. The time-constant by which the super-saturated lithium will precipitate is influenced by the degree of super-saturation, the time and temperature of saturation and by the presence of lattice defects and certain impurities. For example, it has been shown[6] that oxygen and lattice defects will accelerate and copper will retard the precipitation of lithium. The effect of copper is interesting in that it is an interstitial impurity (as is lithium) and has a much higher mobility and lower solubility. Carter and Swalin[6] have shown that copper will precipitate more readily in traps than will lithium. This has the effect of neutralizing or lowering the cross-section of a trap for lithium precipitation, thus increasing the precipitation time-constant. Although it has not been demonstrated, it is probable that nickel will have the same effect as copper in its ability to act as a trap-neutralizing impurity.

DETECTOR FABRICATION

No discussion of the concept of semiconductor impurity compensation by ion-drift will be given as this subject is amply covered in the literature.[8] It is necessary only to adapt the usual procedures for drifting lithium in silicon to the production of thick junctions in germanium.

Before presenting detailed drifting techniques, a word of caution is necessary concerning the handling of large germanium crystals. Large area germanium crystals more than 3 or 4 mm thick are very fragile and easily damaged by small mechanical or thermal shocks. For example, the following treatments have been found to fragment or produce internal cracks: transferring a crystal from boiling to 25°C methyl alcohol; cooling a crystal with adherent nickel or indium amalgam contacts to 77°K; putting a crystal on a hot plate at 400°C to alloy lithium; coating with wax, silicone grease, silicone rubber, or silicone varnish and cooling to 77°K. We have found it to be impossible to cut crystals with 7 cm^2 cross-section in one pass with a diamond saw without damage. The crystals are cut by sawing no more than 0.15" in each pass of the blade. Large crystals gold alloyed to Tantalum or Kovar will fracture at 77°K due to differential contraction but we have successfully cooled crystals alloyed to molybdenum.

The resistivity of the germanium is selected so the lithium drifting can be carried out while operating in the shaded area of Fig. 1. This will insure that the equilibrium ionized lithium concentration is always greater than the acceptor concentration. We have normally used 30 to 45 ohm-cm, gallium doped, zone leveled crystals.[9] Crystals from various sources have been used including zone leveled, vacuum float-zoned and pulled crystals some of which were dislocation free. The pulled crystals which have been used all contained some impurity which rapidly catalyzed the lithium precipitation -- with a time constant of minutes -- while the vacuum float-zoned crystals did not produce junctions after lithium diffusion, probably due to inhomogeneous acceptor distribution. Therefore, the only useful crystals have been zone leveled.

After slicing, the crystals are lapped on both sides with 600 grit alundum, lightly copper plated and heated to 425°C for a few minutes. About 2 μ of lithium metal is evaporated to completely cover one side of the crystal and the lithium is diffused for 5 min. at 425°C. The diffusion is carried out in nitrogen, the crystal being placed on a 1/4" thick graphite pad sitting on a hot plate. The graphite damps the thermal shock of the hot plate. After heating, the crystal and graphite pad are placed on a water cooled copper block. To obtain the highest ionized lithium concentrations it is necessary to cool

as rapidly as possible from the diffusion temperature consistent with avoiding cracking.

To assure that the lithium doped region completely covers one side of the crystal, the four edges are removed by sawing. The crystal is lapped with 600 grit all over, etched for 3 min. in constantly agitated 3:1 HNO_3-HF and the front and back coated completely with Ga-In eutectic (M.P. 15°C) or Hg-In amalgam (M.P. 0°C) and placed lithium side down on the drift apparatus.

The drift apparatus is similar to that of Goulding and Hansen[10] with the exception that no drift monitoring is included. This apparatus and associated circuitry is shown in Figs. 2 and 3. The essential features of this apparatus are that the device is drifted at constant power by using constant voltage and constant current. This condition is maintained by varying the temperature by dissipating power in a heater transistor to maintain the device current at the set value. A variable resistance is inserted in the power supply and this is set to share the supply voltage equally with the device. This allows operation at a power maximum for given control settings. With these controls, the device can be brought to the desired drift conditions and then left unattended indefinitely with no chance of runaway occurring. One drawback of this type of control is that, due to the temperature variation during drifting, calculation of the time dependence of drift depth is made very difficult and it is necessary to determine this depth by probing or staining. In practice the junction depth is determined by probing with a high impedance voltmeter on the side of the device while drifting or by removing the device and staining by reverse biasing in a $CuSO_4$ solution. Some typical drift times are:

1.5 mm -- 2 hrs;
3 mm -- 30 hrs;
6 mm --150 hrs;
and 10 mm --400 hrs.

When the device is first placed on the drift apparatus the temperature is raised to just below the intrinsic temperature as shown in Fig. 1 and the voltage increased slowly so that after about 1 hr. 500 volts is reached. The lithium is now drifting at the maximum rate for 500 volts since the current demand

switch is set to give a temperature just below intrinsic. As drifting proceeds, the temperature will drop due to the current generated in the compensated germanium and the current demand can be increased to maintain near intrinsic temperature. Since lithium compensation cannot occur in the intrinsic temperature region, it is important that this temperature never be attained. As the compensated region becomes thicker, the temperature drop across the germanium becomes greater and this effect must be taken into account when setting the temperature by the current demand switch.

The length of time that drifting can continue is limited only by the time that a surplus of ionized lithium can be maintained in the lithium diffused region. The lithium disappears both by diffusion to the surface where it becomes de-ionized and by precipitation. When using copper doped, high resistivity, zone leveled crystals, it appears that diffusion to the surface is the dominant mechanism that limits drift time. After the initial lithium diffusion and etching, the ionized lithium gives a sheet resistance of about 0.1 $\Omega/\square$ and after drifting for 8 mm the sheet resistance is in the range 0.4 - 1.0 $\Omega/\square$. Frequently the apparent lithium concentration will increase after etching, indicating surface conversion to p-type. If, during drifting, there is a conversion to p-type the temperature will drop for a given current, the electric field will be reduced due to charge injection and the drifting will cease. However, a more serious effect of the lowering of the surface concentration of lithium is the difficulty of making a good ohmic contact to n-type germanium.

Since it is known[11] that, of all the metals, only antimony is ohmic to n-type germanium, about the only methods possible for good ohmic contacts are to have a degenerate n-type surface or to use alloyed or diffused contacts. Due to the difficulties of using a high temperature operation like alloying or diffusing, a high lithium surface concentration must be preserved. In practice, the device is etched after drifting to obtain a more lithium rich surface, a very thin Ga-In contact is applied and the device tested at 77°K. If the leakage current is greater than 10^{-9} amp at 300 volts and 77°K, the device is re-etched until the leakage is less than this value. It sometimes happens that the lithium concentration is not high enough to give an ohmic contact to Ga-In, in which case the device is discarded. Typically, for a device which has been drifted 8 mm, about 3-5 mils of germanium must be removed before

an ohmic contact is achieved. When a device has been drifted only 3-4 mm the surface is usually still strongly enough n-type that no etching is needed.

The capacitance of the devices when measured at audio frequencies at 77°K is usually 2 to 3 times greater than would be calculated from the known drift depth. This effect indicates the presence of a strong surface depletion layer as the result of etching. When the device is given a short wash with 30% H_2O_2 the capacitance is only about 20% too high — indicating probably a slight surface accumulation. In practice, all devices are given the H_2O_2 treatment before use.

RESULTS

A typical crystal holder is shown in Fig. 4. Electrical contacts are made by a very thin layer of Ga-In entectic and thermal contact by a layer of Dow Corning 200 fluid, viscosity 1,000,000 cps. Figs. 5-7 show spectra obtained with lithium drifted germanium crystals using the amplifier described in Ref. 10. The dimensions of the crystal used in Fig. 5 was 2 cm x 3 cm x 0.8 cm and that of Figs. 6 and 7 2 cm x 1 cm x 0.8 cm. Energy resolution in $(F.W.H.M.)^2$ is plotted against energy in Fig. 8. The fact that the experimental points form a straight line would indicate that the only noise sources in this case are electronics and the statistics of charge collection. Fig. 9 shows an uncollimated C^{137} source illuminating the side of a 1 cm x 2 cm x 8 mm detector. Tailing and line broading on the electron peaks is apparent — probably due to charge collected from a low field region or from an entrance window.

No experiments have been done which would indicate the lifetime of these detectors under various ambient temperatures. One detector has been in use for seven months at 77°K with no deterioration and several have been stored at -60°C for several month periods with no apparent ill effect.

ACKNOWLEDGMENTS

We would like to thank Dave Shirley, Jack Hollander and Stan Thompson for their help in measuring the performance of devices and for providing the Lu^{177} and Co^{60} spectra. Much of what is in this paper has benefited from the continuous interest and contributions of F. S. Goulding.

FOOTNOTE AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission.

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   b) Semiconductor Nuclear Particle Detectors, National Academy of Sciences Publication #871 (1961).

   c) Nuclear Electronics, International Atomic Energy Agency, Vienna, 1962.

9) Sylvania Electric Co., Towanda, Penn.

10) F. S. Goulding and W. L. Hansen, "An Automatic Lithium Drifting Apparatus for Silicon and Germanium Detectors", Proceedings of the Ninth Semiconductor and Scintillation Counter Symposium, IEEE Transactions on Nuclear Science, June 1964.

11) E. C. Wurst and E. Borneman, J. Appl. Phy. 28, 235 (1957).

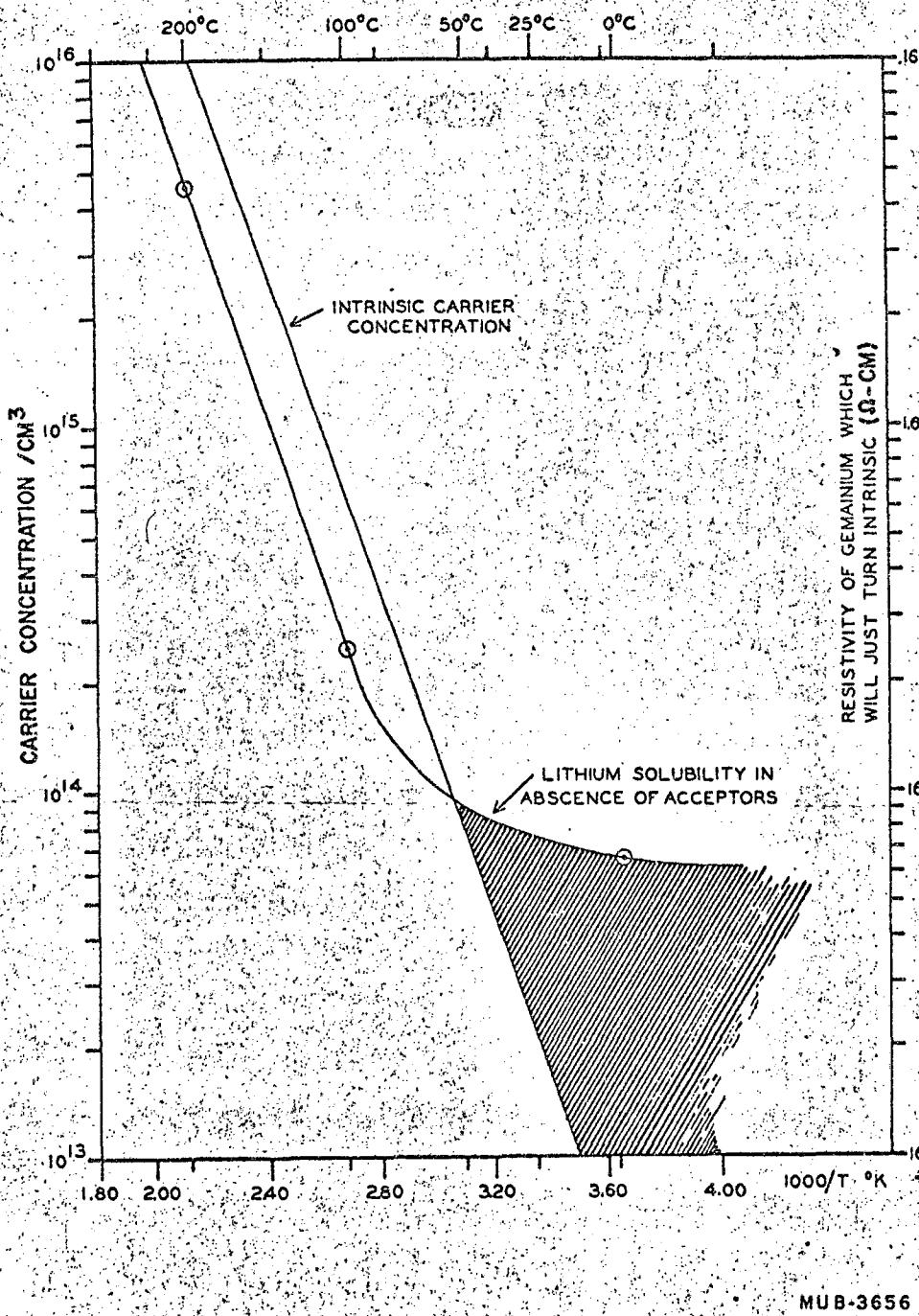
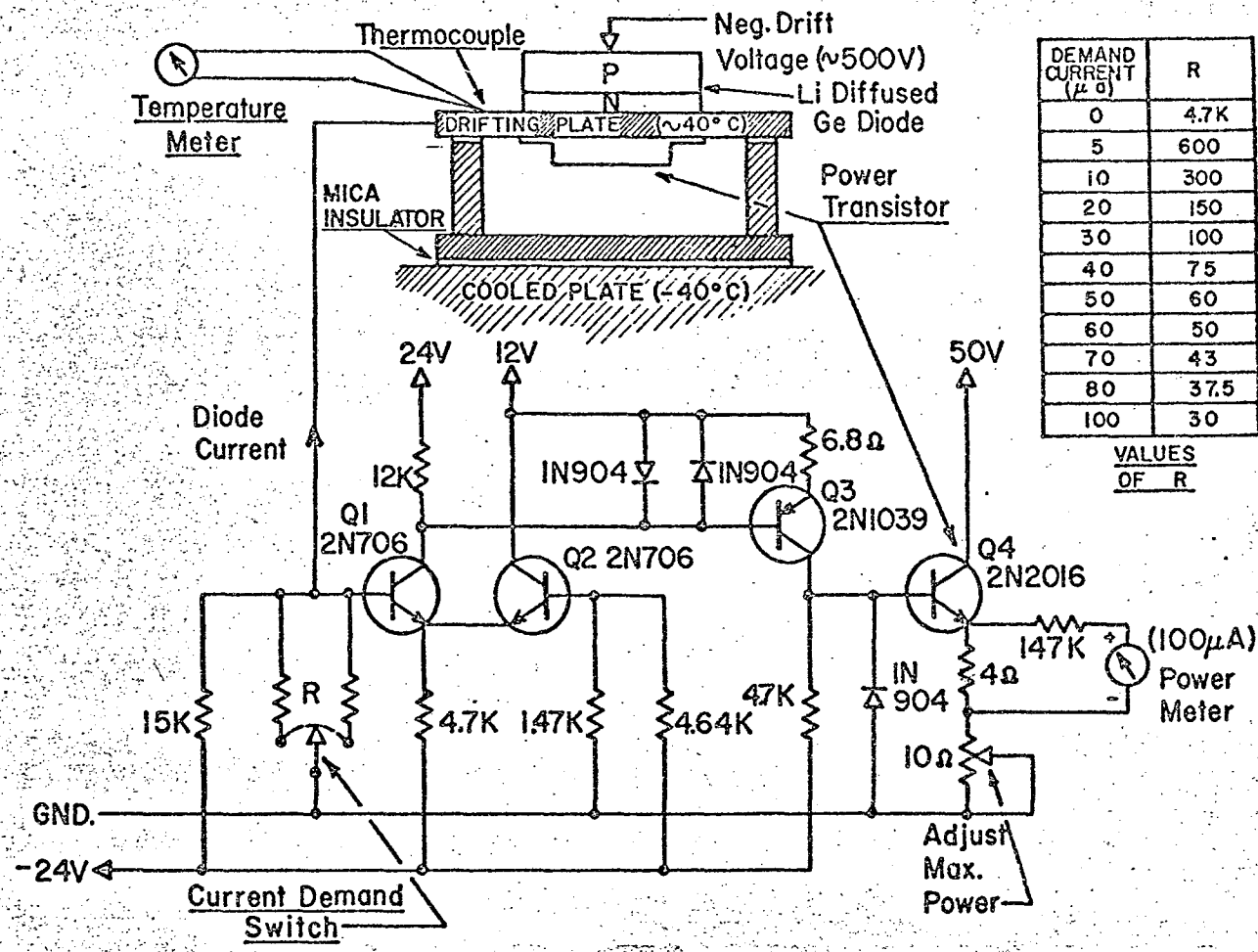


Fig. 1. Lithium solubility in absence acceptors and intrinsic carrier concentration in germanium plotted vs. reciprocal temperature.



DEMAND CURRENT (μa)	R
0	4.7K
5	600
10	300
20	150
30	100
40	75
50	60
60	50
70	43
80	37.5
100	30

VALUES OF R

Fig. 2. GERMANIUM LITHIUM DRIFTING CONTROLLER

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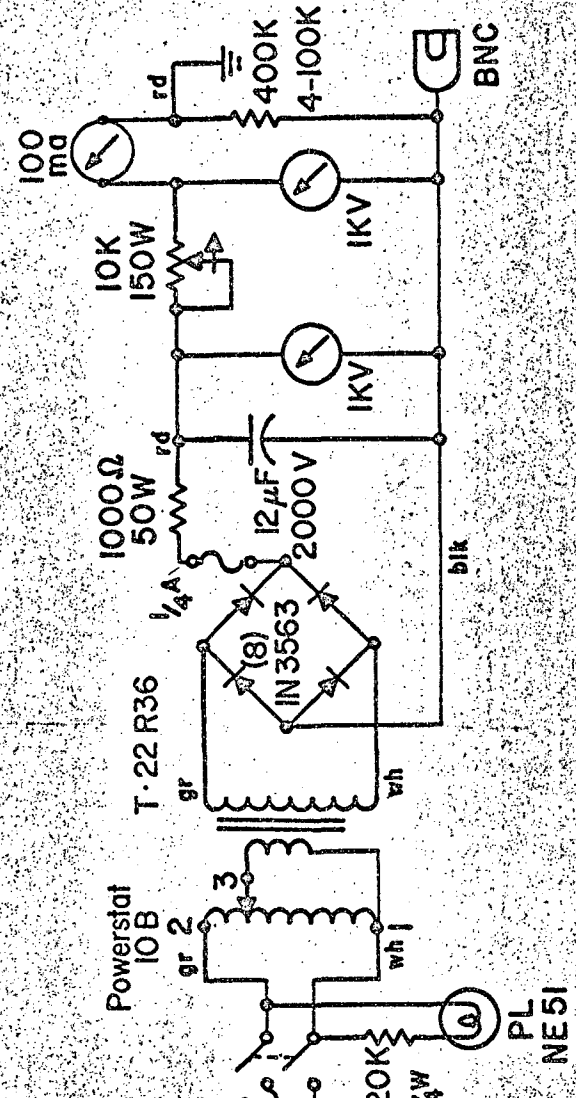

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Fig. 3. 1000 Volt - 100 ma Power Supply

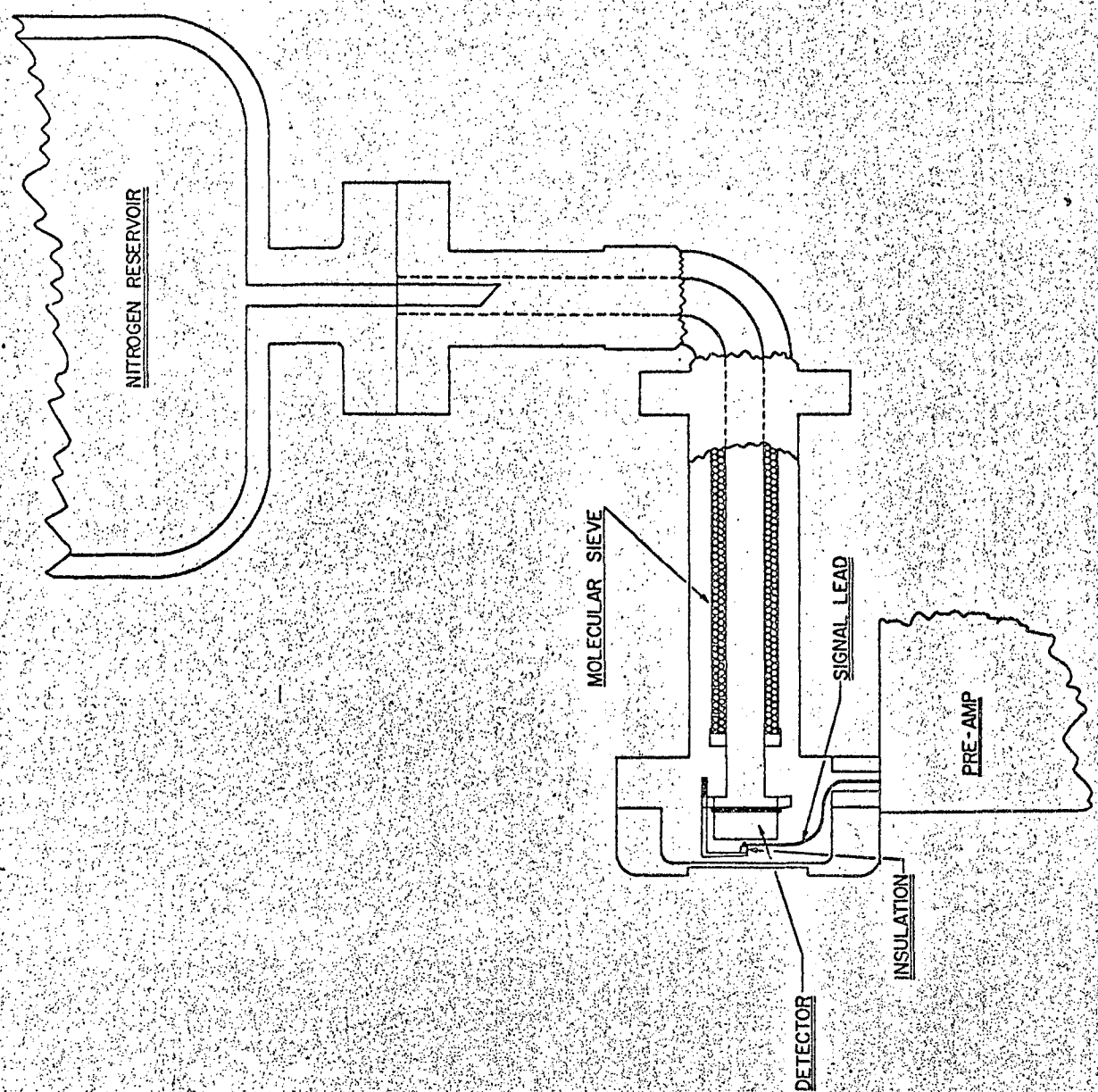

Fig. 4. Typical detector holder.

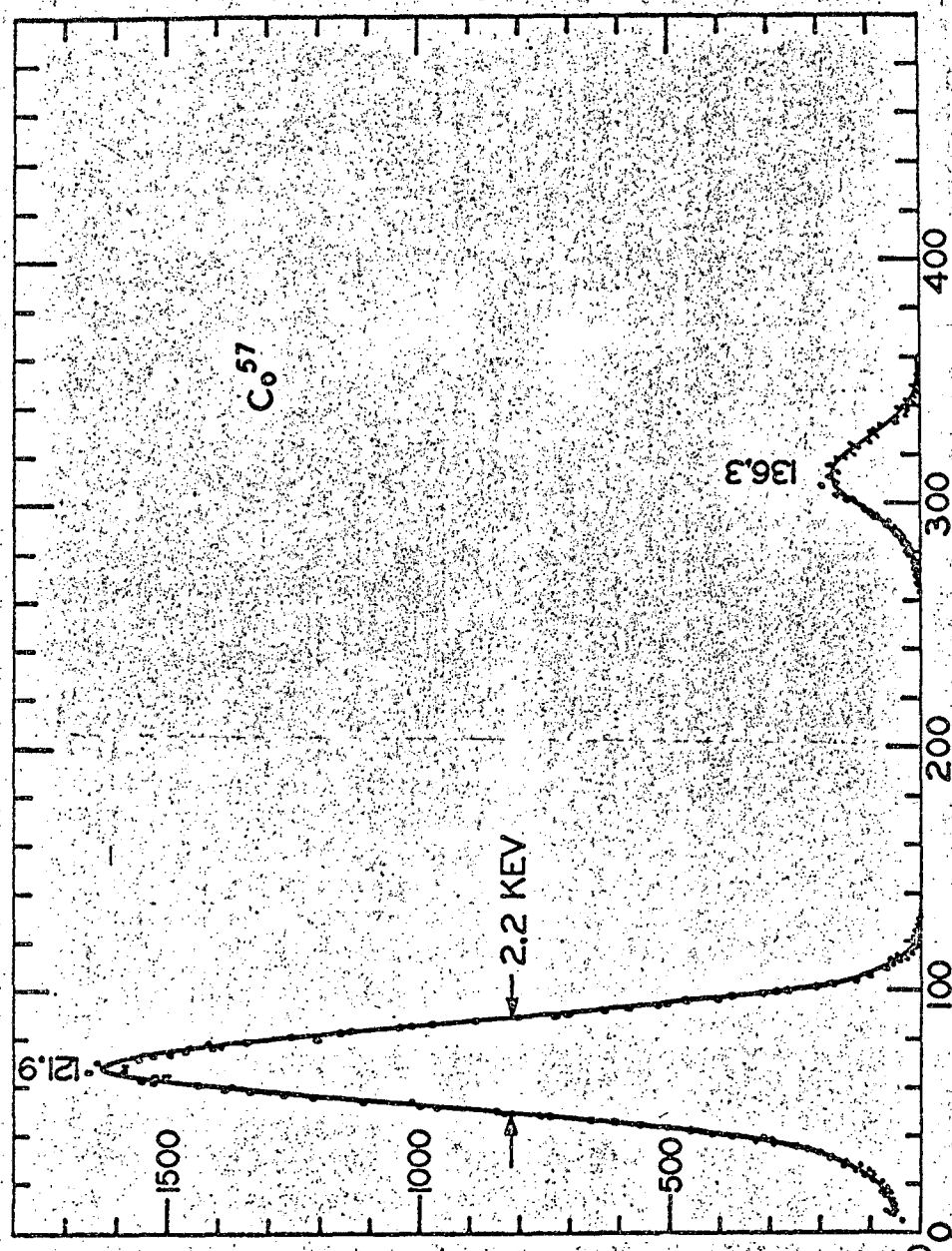

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Fig. 5. Co^{57} γ-rays using 3cm x 2cm x 8mm detector.

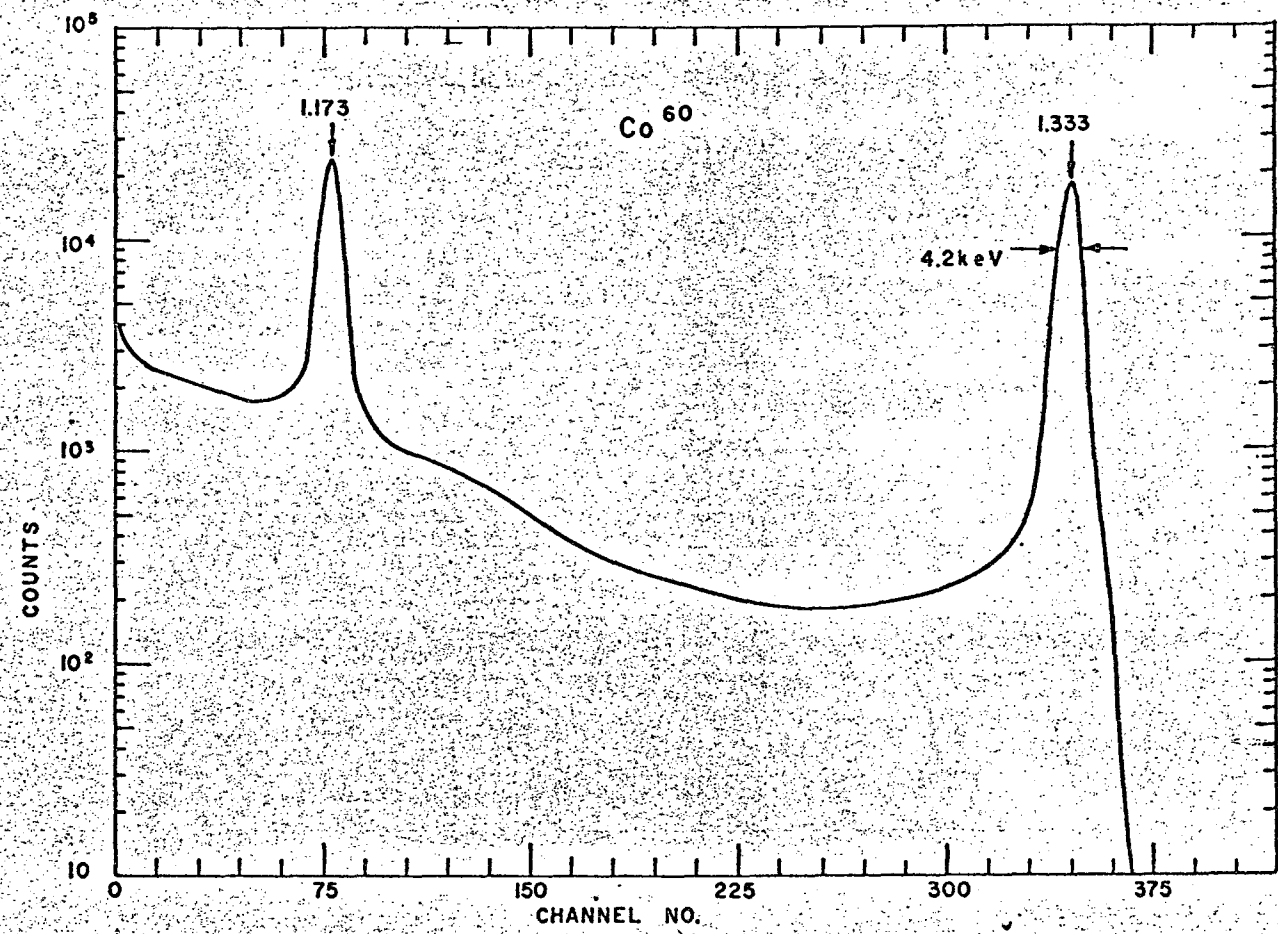

Fig. 6. Co^{60} γ-rays using 2 cm x 1cm x 8mm detector.

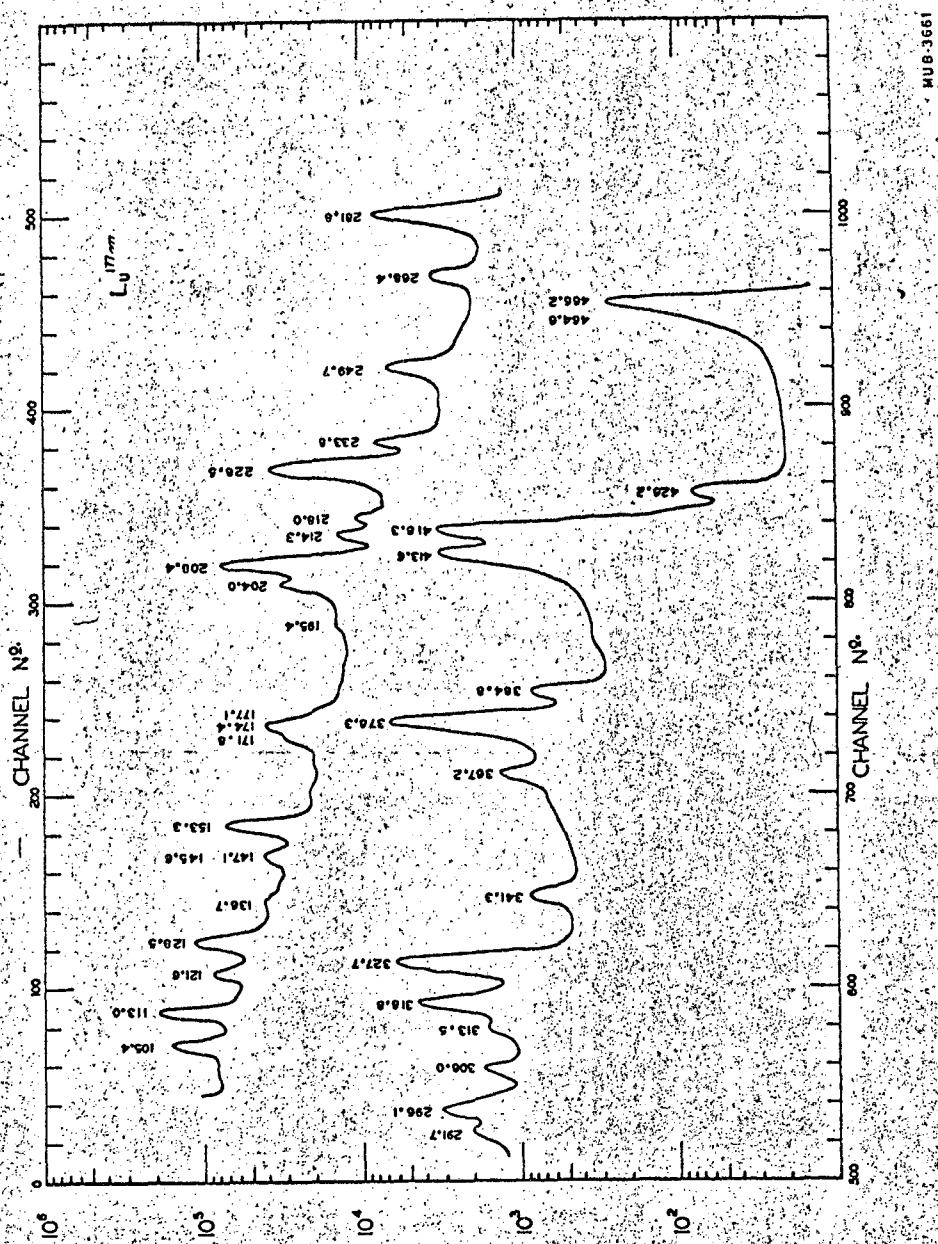

Fig. 7. Lu 177m γ-rays using 2cm x 1cm x 8mm detector.

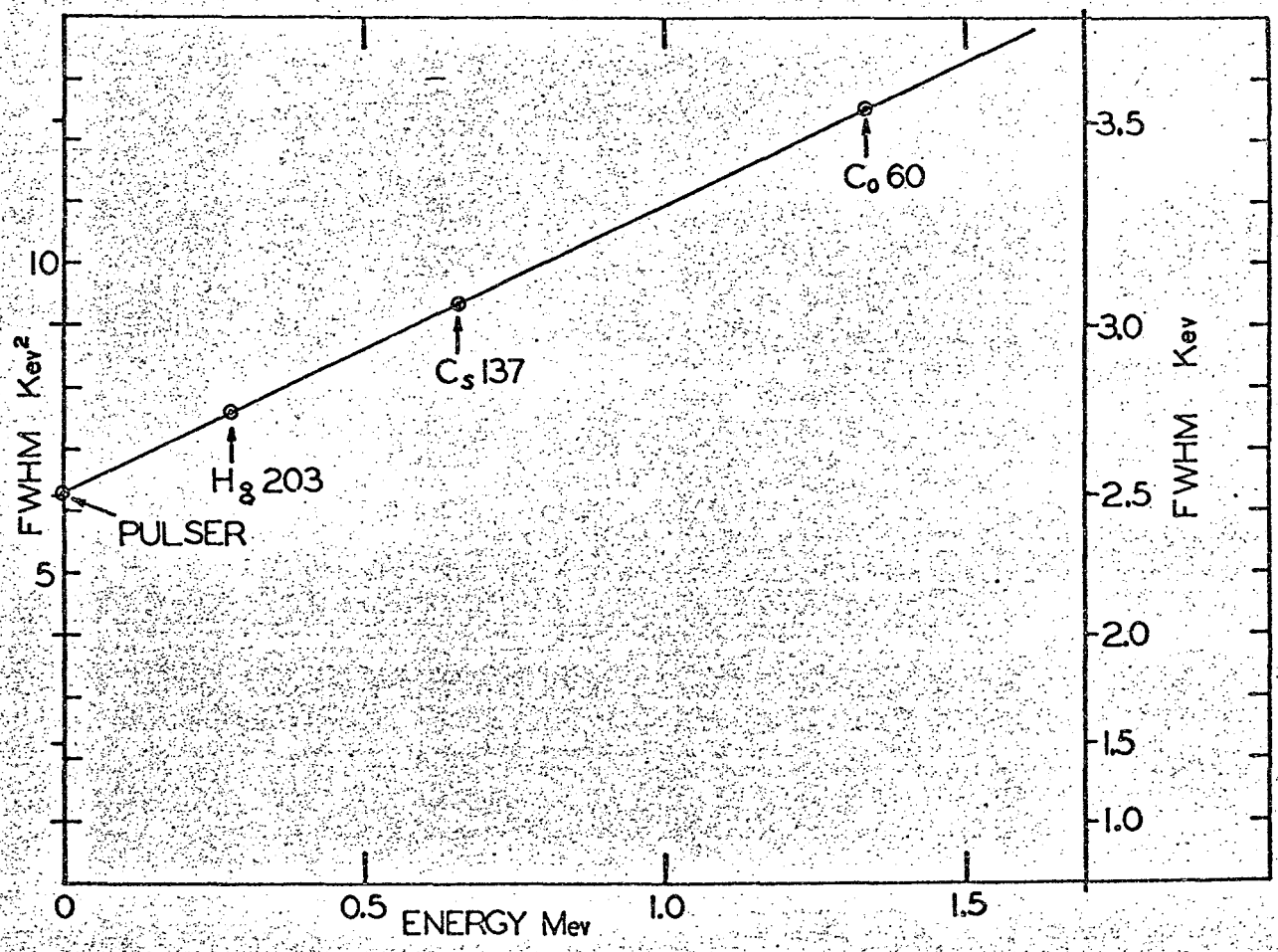

Fig. 8. γ-ray energy resolution in FEHM in keV^2 plotted vs energy for 2cm x 1cm x 8mm detector.

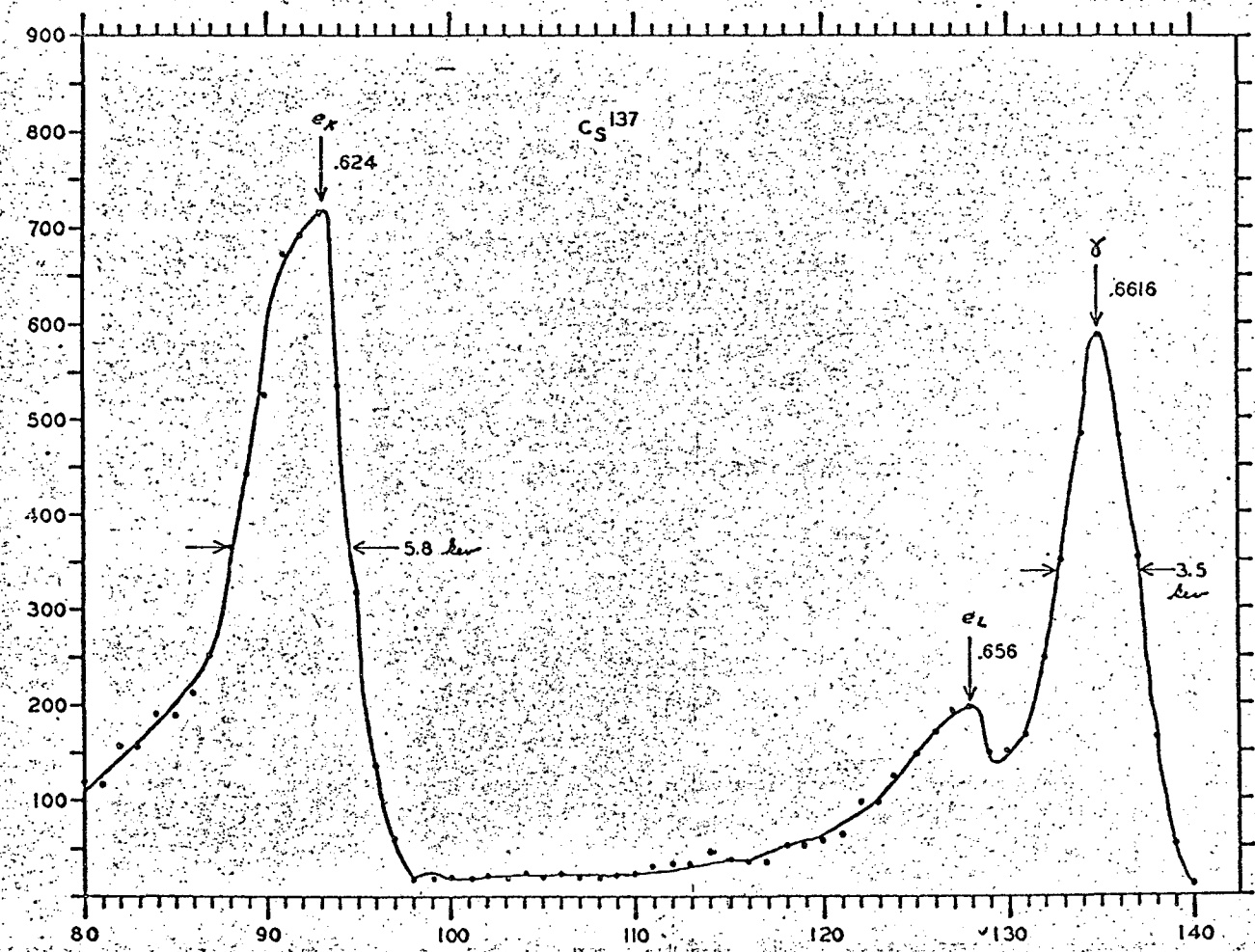

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Fig. 9. γ-rays and conversion electrons of Cs^{137} from the side of a 2cm x 1cm x 8mm detector -- uncollimated.

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